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**THE CATALYTIC HYDROLYSIS OF  
p-NITROPHENYLDIPHENYL PHOSPHATE IN A  
CTAB MICROEMULSION**

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## PREFACE

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# The Catalytic Hydrolysis of p-Nitrophenyldiphenyl Phosphate in a CTAB Microemulsion

## 1 INTRODUCTION

During the past decade, mechanistic studies of several phosphate and phosphonate esters have been reported. These substances are known to be acetylcholine esterase inhibitors and are useful in mechanistic studies of enzyme action.<sup>1</sup> Additionally, their related neurotoxicity makes them important as pesticides,<sup>2</sup> and their decomposition is similarly important. Since these phosphates are normally only slightly soluble in water, micellar and microemulsion media have often been employed in mechanistic investigations.<sup>3,4</sup> Under these conditions enhancements are observed in both solubilization and in the rate of decomposition. This "micellar catalysis" is thought to involve a local increase in the concentrations of the reactive species at the micellar surface.

One particularly interesting adaptation of this micellar approach is the use of 2-iodosobenzoic acid (IBA) and its derivatives as nucleophilic catalysts in phosphate ester decomposition. The work by Moss and co-workers<sup>5</sup> employed both IBA, its 5-octoxy- and surfactant functionalized derivatives in an aqueous cetyltrimethylammonium chloride (CTAC) micellar medium. Their data strongly indicate that, at least in a micellar medium, IBA accelerates the rate of ester decomposition without being consumed.

The peculiarities in the structure of IBA undoubtedly contribute to its catalytic activity. X-ray studies<sup>6,7</sup> indicate that as the crystalline sodium salt it exists in the bicyclic form **1b** (Scheme I of Figure 1). In solution the  $pK_a$  of IBA is 7.02 (in our hands, by titrimetry). This is a strong indication that the "normal" IBA structure (**1a**) is unfavorable in solution as well since (1) the upper limit for  $pK_a$  values for substituted benzoic acids is about 5.5, and (2) the iodoso substituent should be electron-withdrawing and thus monocyclic IBA, **1a**, should have a  $pK_a$  less than 4.2, the  $pK_a$  of unsubstituted benzoic acid.

The accepted mechanism for the uncatalyzed hydrolysis of PNDP, although it has not been definitively proven, involves attack of nucleophile  $X^-$  on PNDP, accompanied or followed by expulsion of the 4-nitrophenoxide ion,<sup>8,9</sup> illustrated in Scheme II of Figure 1. In the presence of catalyst IBA the mechanism is believed to involve attack of IBA on phosphorus followed by release of 4-nitrophenoxide. Regeneration of the catalyst involves nucleophilic attack on the IBA-phosphate intermediate, as shown in Scheme III (Figure 1).

$$\text{1a} \rightleftharpoons \text{1b} \xrightleftharpoons[\text{+H}^+]{\text{-H}^+} \text{1c}$$

Chemical reaction scheme showing the nucleophilic attack of an anion  $X^-$  on the central phosphorus atom of a triphenyl phosphite. The phosphite has one phenyl group and one p-nitrophenyl group. The reaction yields a phosphine oxide salt ( $X-P(=O)(Ph)_2$ ) and a p-nitrophenoxide ion ( $O^-Ph-NO_2$ ).

The reaction scheme illustrates the mechanism of iodine(III) catalyzed hydrolysis of a phosphonate ester. The process begins with the deprotonation of a phosphonate ester by a base ( $\text{OH}^-$ ) to form a phenoxide intermediate. This intermediate then undergoes nucleophilic attack on the iodine atom of an iodo-substituted phosphonate, displacing a phenoxide group. The resulting intermediate then undergoes further rearrangement and elimination to yield the final products: a carboxylic acid and a phosphonate ester.

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We have extended this work to microemulsion media by examining the decomposition of 4-nitrophenyldiphenyl phosphate (PNDP) in a hexadecane/water microemulsion stabilized by cetyltrimethylammonium bromide (CTAB) and 1-butanol. This medium was chosen because it was previously used in the absence of IBA<sup>8</sup> and thus serves as a base line for the catalytic investigations.

## 2 EXPERIMENTAL SECTION

Cetyltrimethylammonium bromide (CTAB) was purchased from Aldrich. Microemulsions prepared from this material as received gave kinetic data indistinguishable from microemulsions which had been prepared from CTAB recrystallized from methanol. The 1-butanol and *n*-hexadecane were Aldrich reagent grade and were used as received. The iodosobenzoic acid (IBA) was obtained from Sigma and used as supplied. The aqueous phase was 0.03 M borate buffer prepared by using sodium tetraborate decahydrate ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , Baker Reagent) and deionized, glass-distilled water. In most of the experiments a microemulsion consisting of 18% (by mass) CTAB, 18% 1-butanol (cosurfactant), 4% *n*-hexadecane (oil), and 60% aqueous buffer was used. The pH values reported are those determined directly in the microemulsion, the pH of which was generally 0.2 unit higher than the aqueous buffer from which it was prepared.<sup>10</sup> The initial concentration of PNDP was normally  $5.44 \times 10^{-5}$  M. Experiments designed to give the hydroxide rate constant employed microemulsions prepared (and titrated) in the range of  $1.2 \times 10^{-3}$  to  $1 \times 10^{-2}$  M in NaOH.

Reactions were followed by monitoring the absorbance of the product, 4-nitrophenoxide ion, at 402 nm with either a Hewlett-Packard 8450A photodiode array spectrophotometer or a Gilford 2400S spectrophotometer equipped with a thermostated four-cell carriage and cell positioning programmer. The Gilford 2400S spectrophotometer was interfaced to an Apple IIe computer via an Adalab Interface card for "real time" data acquisition. Temperature control ( $25 \pm 0.1$  °C) was achieved by use of an Endocal RTE-8DD controlled bath.

Rate constants were generated on an Apple IIe microcomputer using a weighted linear least-squares technique applied to the data in the  $\ln (A_{\text{inf}} - A_t)$  vs time form. Individual weights were calculated by using a linear-to-log transform procedure.<sup>11</sup>

The pH measurements were performed by using a glass electrode with an Orion or Fisher pH meter, calibrated with standard buffers at pH values of 4.00, 7.00, and 10.00, also obtained from Fisher.

### 3 RESULTS AND DISCUSSION

The decomposition of PNDP in aqueous or largely aqueous media can be reasonably expected to follow a rate law of the form:

$$\begin{aligned}\text{rate} &= k_{\text{hyd}} [\text{PNDP}] + k_{\text{OH}} [\text{OH}^-] [\text{PNDP}] + k_{\text{IBA}} [\text{IBA}] [\text{PNDP}] \\ &= \{ k_{\text{hyd}} + k_{\text{OH}} [\text{OH}^-] + k_{\text{IBA}} [\text{IBA}] \} [\text{PNDP}]\end{aligned}\quad (1)$$

where the term  $k_{\text{hyd}}[\text{PNDP}]$  represents the hydroxide independent "background" reaction, the  $k_{\text{OH}}[\text{OH}^-][\text{PNDP}]$  term represents the second-order reaction between  $\text{OH}^-$  and PNDP, and the  $k_{\text{IBA}}[\text{IBA}][\text{PNDP}]$  term represents the rate enhancement resulting from the addition of IBA to the system. By appropriately choosing the experimental conditions, each of these microscopic rate constants were independently determined.

In order to obtain the  $k_{\text{IBA}}$  value, experiments were run at several buffered pH values. Under these conditions the first two terms of equation 1,  $k_{\text{hyd}} + k_{\text{OH}}[\text{OH}^-]$ , are constant. If, as Moss *et al.* suggest,<sup>12</sup> IBA is not consumed in the reaction, then the third term is also constant, and Equation 1 reduces to a description of an experimentally first-order process:

$$\text{rate} = k_{\text{obsd}} [\text{PNDP}] \quad (2)$$

where

$$k_{\text{obsd}} = k_{\text{hyd}} + k_{\text{OH}} [\text{OH}^-] + k_{\text{IBA}} [\text{IBA}] \quad (3)$$

Figure 2 shows plots of absorbance-time data at several different IBA concentrations in the microemulsion system. The lines drawn through the points are theoretical lines assuming simple first-order kinetics as in equation 2. Figure 3 shows the same data plotted as  $\log (A_{\text{inf}} - A_t)$  vs. time. Such linearity was normally observed for five or more half-lives indicating no significant deviation from first-order behavior. This is evidence that IBA is a "turn-over" catalyst.

A plot of  $k_{\text{obsd}}$  vs.  $[\text{IBA}]$  at pH 8.5 yields a straight line (Figure 4) as predicted by equation 3 having a slope equal to  $k_{\text{IBA}}$  and an intercept equal to  $k_{\text{hyd}} + k_{\text{OH}}[\text{OH}^-]$ .

To ensure that the preliminary analysis was valid, we collected similar data at pH values of 9.2, 9.8, and 10.5. The value of  $k_{\text{IBA}}$  should be independent of pH since the  $\text{pK}_a$  of IBA is 7.02 and, therefore, is fully ionized at each of the pHs under study.

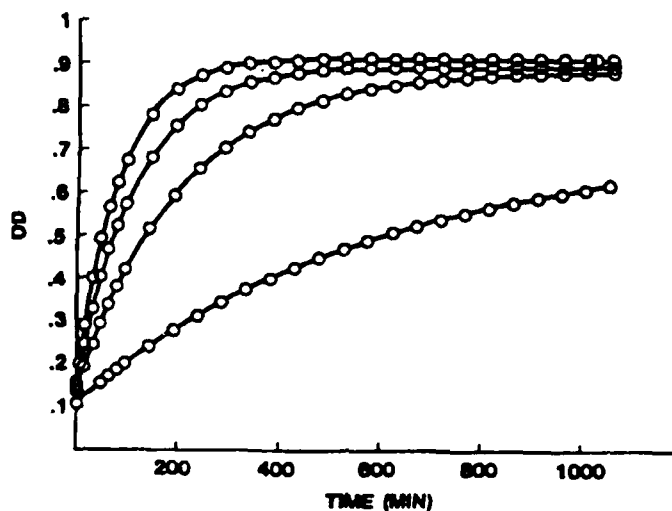


Figure 2. A Plot of Absorbance of 4-Nitrophenoxide vs Time at pH 9.2 and at Varying Values of [IBA]; the Solid Lines are Calculated on the Assumption of First-Order Behavior

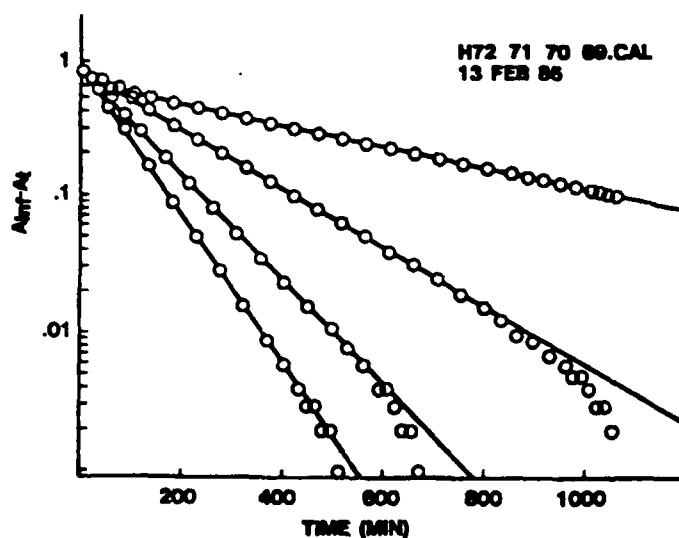


Figure 3. A Plot of the Log ( $A_{inf} - A_t$ ) vs Time Obtained by Using the Data of Figure 2. Note that First-Order Behavior is Exhibited for Several Half-Lives.

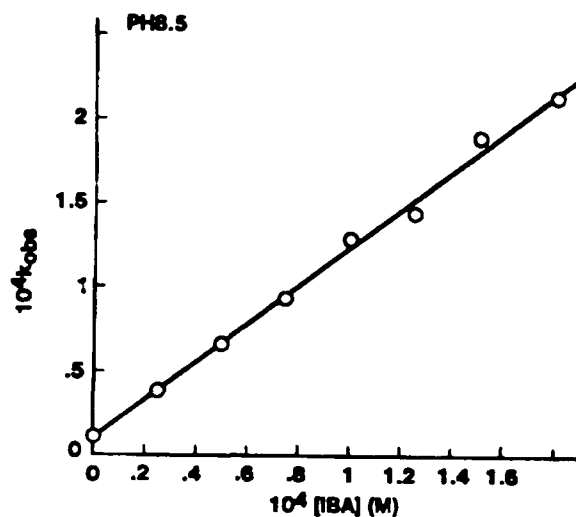


Figure 4. The Plot of  $k_{obsd}$  Vs [IBA] (Linear at pH 8.5 and at All pHs Examined). The Slope of the Line is Equal to  $k_{IBA}$ ; the Intercept Equals  $k_{hyd} + k_{OH} [OH^-]$ .

The values of  $k_{IBA}$  and  $(k_{hyd} + k_{OH}[OH^-])$ , as determined from analyses of at least eight experiments at each pH, are presented in Table 1. Since the errors in the slopes of the plots of  $k_{obsd}$  vs. [IBA] are in the range of 2 to 5%, these data present no evidence of any variation in  $k_{IBA}$  in the pH range 8.5 to 10.5. The average value of the slopes (and the average value of  $k_{IBA}$ ) is  $1.22 \pm 0.07 \text{ M}^{-1}\text{s}^{-1}$ .

In order to get more reliable values for  $k_{hyd}$  and  $k_{OH}$ , microemulsions were prepared with standard NaOH solution containing no catalyst as the aqueous phase. Kinetic experiments were performed with  $[OH^-]$  varying from  $1.20 \times 10^{-3}$  to  $1.00 \times 10^{-2} \text{ M}$ . Since there is no IBA present, equation 1 becomes:

$$\text{rate} = k_{hyd} [\text{PNDP}] + k_{OH} [OH^-] [\text{PNDP}] \quad (4)$$

or

$$\text{rate} = k_{obsd} [\text{PNDP}]$$

where

$$k_{obsd} = k_{hyd} + k_{OH} [OH^-] \quad (5)$$

Table 1. Effect of pH on  $k_{OH}$  and  $k_{IBA}$  in CTAB Microemulsion at 25 °C

pH	$\frac{k_{hyd} + k_{OH} [OH^-] \times 10^5}{s^{-1}}$	$\frac{k_{IBA}}{s^{-1} M^{-1}}$
8.5	$0.93 \pm 0.28$	$1.14 \pm 0.03$
9.2	$2.52 \pm 0.22$	$1.31 \pm 0.03$
9.8	$4.05 \pm 0.51$	$1.24 \pm 0.05$
10.5	$4.84 \pm 0.51$	$1.18 \pm 0.03$

Since we used a high excess of  $[OH^-]$  in these experiments, the rate law was pseudo first order. Figure 5 depicts the dependence of  $k_{obsd}$  on  $[OH^-]$ . The least-squares slope of this line is equal to  $k_{OH}$  with a best fit value of  $0.145 M^{-1}s^{-1}$ , which is in good agreement with the value extracted from previously published data.<sup>8,13</sup> The intercept,  $k_{hyd}$ , is  $5 \times 10^{-6}$ , which is indistinguishable from zero for these data. Hence, equation 1 may be written as:

$$\text{rate} = \{0.145 [OH^-] + 1.22 [IBA]\} [PNDP] \quad (6)$$

Analogous experiments were performed in aqueous solution for comparison. The results from studies of buffered solutions (again for the determination of  $k_{IBA}$ ) are listed in Table 2, and the results from studies of NaOH solutions (for the determination of  $k_{hyd}$  and  $k_{OH}$ ) are in Table 3. The value of  $k_{IBA}$  in aqueous solution is smaller than in the microemulsion and has a slight, but real, dependence on pH while  $k_{OH}$  is  $0.437 M^{-1}s^{-1}$ .

The initial work by Moss et al.<sup>5,11</sup> gave observed rate constants as a function of [CTAC]. We chose to expand this work to measure second-order rate constants for direct comparison. Four different micellar CTAC solutions were employed and kinetic experiments were performed at four IBA concentrations in each of these media, thus allowing the determination of both  $k_{IBA}$  and the combined  $k_{hyd} + k_{OH} [OH^-]$  terms at each CTAC concentration. All runs were buffered with 0.03 M borate at pH 9.2. The results summarized in Table 4 show that  $k_{IBA}$  decreases with increasing [CTAC], which is the expected result above the critical micelle concentration (cmc).

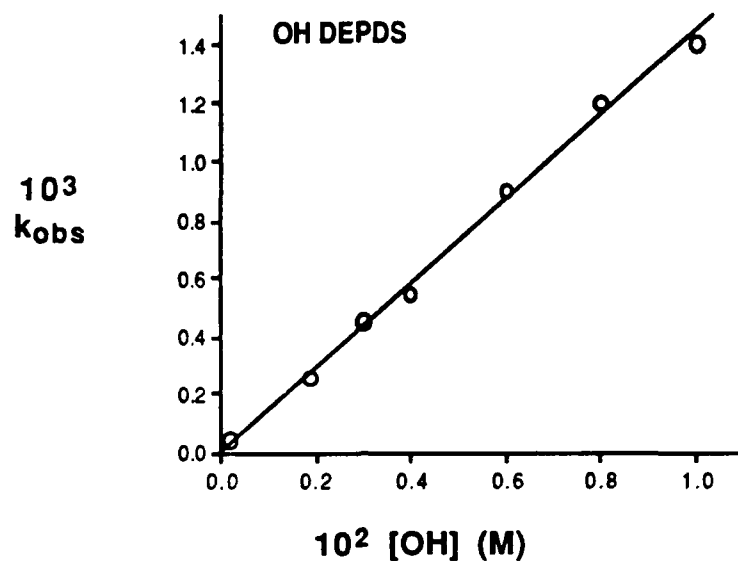


Figure 5. A Plot of  $k_{\text{obsd}}$  vs  $[\text{OH}^-]$  in the Absence of IBA. The slope equals  $k_{\text{OH}}$ , since  $k_{\text{hyd}} \sim 0$ .

Table 2. Values of the Rate Constants in Aqueous Borate Buffer Solutions, at 25 °C

pH	$\frac{k_{\text{hyd}} + k_{\text{OH}} [\text{OH}^-]}{\text{s}^{-1}}$	$\frac{k_{\text{IBA}}}{\text{s}^{-1} \text{ M}^{-1}}$
8.5	$(5.38 \pm 0.22) \times 10^{-5}$	$0.519 \pm 0.021$
9.2	$(6.28 \pm 0.46) \times 10^{-5}$	$0.675 \pm 0.038$
10.4	$(2.03 \pm 0.06) \times 10^{-4}$	$0.798 \pm 0.045$



**Table 3. Effect of  $\text{OH}^-$  and  $k_{\text{obsd}}$  in Aqueous Solution in the Absence of IBA, at 25 °C**

$10^2 [\text{OH}^-]$	$10^3 k_{\text{obsd}} / \text{s}^{-1}$
1.00	$4.16 \pm 0.03$
0.75	$3.17 \pm 0.01$
0.50	$1.98 \pm 0.01$
0.25	$0.97 \pm 0.03$

In order to demonstrate unambiguously that IBA is indeed a turnover (rather than stoichiometric) catalyst in the CTAB microemulsion medium two additional experiments were performed. In the first of these, the PNDP concentration was increased such that the ratio of PNDP to IBA was 115 to 1 at a pH of 9.5. In order to study this reaction spectrophotometrically, data were taken at 470 nm where the extinction coefficient of 4-nitrophenoxide is only  $763 \text{ M}^{-1}\text{cm}^{-1}$ . Normal first-order kinetics were observed with a calculated rate constant consistent with equation 6. In addition, if IBA were consumed in the reaction it would be quickly depleted and limited rate enhancement would be observed. (It should be pointed out that we did not observe "burst kinetics" in this or any other experiment.<sup>5a</sup>)

The second experiment involved repeated addition of PNDP to the same reaction mixture. In the first step, PNDP was added to the microemulsion containing IBA and the kinetics carefully followed. After ten half-lives, a second addition of PNDP was added to the same solution and kinetics were again followed. The first-order rate constants obtained from both segments of the reaction were identical within experimental error, indicating that the first reaction had no effect on the IBA concentration.

**Table 4. Effect of CTAC on  $k_{\text{OH}}$  and  $k_{\text{IBA}}$  in Aqueous Micellar Solution, at 25 °C**

CTAC M <sup>-1</sup>	$k_{\text{hyd}} + k_{\text{OH}}[\text{OH}^-] \times 10^{-3}$ s <sup>-1</sup>	$10^{-3} k_{\text{IBA}}$ s <sup>-1</sup> M <sup>-1</sup>
0.82	$2.20 \pm 0.02$	$1.55 \pm 0.05$
1.22	$2.04 \pm 0.15$	$1.45 \pm 0.06$
2.03	$2.00 \pm 0.01$	$1.13 \pm 0.02$
2.82	$1.96 \pm 0.01$	$1.10 \pm 0.02$

#### 4 CONCLUSION

The introduction of IBA into the CTAB microemulsion increases the reaction rate by a factor of 10 above background hydrolysis. In addition, the catalyzed rate in CTAB microemulsion is approximately twice the value in water. There is no doubt that IBA functions as a true catalyst; in our experiments we obtained an average turnover number of 25 with no indication of loss of catalytic behavior in CTAB microemulsions. We should indicate that none of our observations are inconsistent with the mechanisms which have previously been proposed for either the catalyzed or the uncatalyzed reaction.<sup>5,8,9</sup>

Examination of the results of our studies and of the studies reported in the literature proves that the CTAC and CTAB micellar solutions are truly remarkable media. Second-order rate constants for the hydrolysis catalysts IBA and its derivatives are at least 1000 times greater in these micellar solutions than in any of the other media studied.<sup>4,5</sup> Further studies of these hydrolysis reactions should be aimed at determining the structural feature(s) of micellar solutions which make them catalytic media. Perhaps then it will be possible to combine the good solubilization properties of microemulsions with the catalytic properties of micellar solutions to produce an ideal medium.

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